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The growth kinetics of $Si_{1-x}Ge_x$ layers from germane and silane

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Abstract. In the present paper we offer a model of the growth kinetics of $Si_{1-x}Ge_x$ layers from silane and germane molecular flows. The model considers disintegration of silane and germane molecules from chemisorption to formation of Si and Ge adatoms and their embedding in a crystal lattice. The numerical modeling of the epitaxial process has shown good agreement with the experimental data and has allowed to explain peculiarities of the experimental dependencies. The effective frequencies of SiH_3 and SiH_2 disintegration for the considered epitaxial method were estimated.
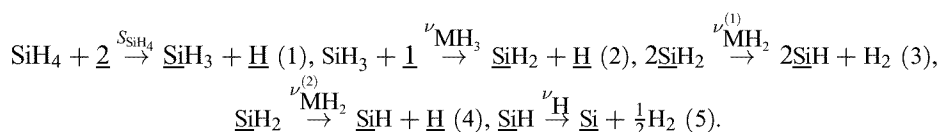
Introduction

In the last decade the chemical vapour deposition from silicon and germanium hydrides at low pressures has been actively used for $Si_{1-x}Ge_x$ layer epitaxy. Despite the large number of experimental works the number of theoretical researches is insignificant, and the available models describe experimental data inadequately. Therefore, as remarked by L. T. Vinh with co-workers "improved models thus seem to be indispensable" [1]. The not good enough agreement of the theory and experiment is possible connected to an extremely simplified consideration of chemical processes on a growing surface. On the other hand, a detailed description of the kinetics of surface reactions inevitably will result in an increase of a number of parameters describing the rates of elementary processes. The task is complicated also by that the values of the majority of rate constants disintegration of SiH_n and GeH_n molecules, unfortunately, are unknown.

In the present paper we offer a model of the growth kinetics of $Si_{1-x}Ge_x$ layers from silane and germane molecular flows. The model considers disintegration of silane and germane molecules from chemisorption to formation of Si and Ge adatoms and their embedding in a crystal lattice. Using the published experimental data, on the basis of the model we have made estimations of rate constants of disintegration of SiH_3 and SiH_2 molecules.

1 Model

A comprehensive analysis of the process of disintegration of SiH_n molecules on a surface $Si(100)$ is made by S. M. Gates with co-workers [2]. They found out that the complete mechanism of silane disintegration is reactions:

$$SiH_4 + 2\underline{} \overset{S_{SiH_4}}{\rightarrow} \underline{Si}H_3 + \underline{H} \ (1), \ SiH_3 + \underline{1} \overset{\nu''_{MH_3}}{\rightarrow} \underline{Si}H_2 + \underline{H} \ (2), \ 2\underline{Si}H_2 \overset{\nu^{(1)}_{MH_2}}{\rightarrow} 2\underline{Si}H + H_2 \ (3),$$

$$\underline{Si}H_2 \overset{\nu^{(2)}_{MH_2}}{\rightarrow} \underline{Si}H + \underline{H} \ (4), \ \underline{Si}H \overset{\nu''_H}{\rightarrow} \underline{Si} + \tfrac{1}{2}H_2 \ (5).$$

Taking into account a chemical similarity of SiH_4 and GeH_4 molecules it is possible to expect that the disintegration of germane will occur by an analogous way [3]. If on a growing surface there are SiH_2 and GeH_2 molecules, these molecules possibly can react by the reaction:

$$\underline{SiH_2} + \underline{GeH_2} \xrightarrow{\nu''^{(3)}_{MH_2}} \underline{SiH} + \underline{GeH} + H_2 \ (6).$$
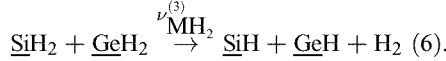
An appropriate system of kinetic equations for dimensionless average concentrations of adsorbed particles is ($M = Si, Ge$):

$$\frac{\partial \theta_{MH_3}}{\partial t} = 2 \frac{S_{MH_4} F_{MH_4}}{N_s} \theta_{nbl}^2 - 2\nu_{MH_3} \theta_{MH_3} \theta_v,$$

$$\frac{\partial \theta_{MH_2}}{\partial t} = 2\nu_{MH_3} \theta_{MH_3} \theta_v - 4\nu_{MH_2}^{(1)} \theta_{MH_2}^2 - 2\nu_{MH_2}^{(2)} \theta_{MH_2} \theta_v - 2\nu_{MH_2}^{(3)} \theta_{SiH_2} \theta_{GeH_2},$$

$$\frac{\partial \theta_{MH}}{\partial t} = 4\nu_{MH_2}^{(1)} \theta_{MH_2}^2 + 2\nu_{MH_2}^{(2)} \theta_{MH_2} \theta_v + 2\nu_{MH_2}^{(3)} \theta_{SiH_2} \theta_{GeH_2} - \nu_{MH} \theta_{MH},$$

$$\frac{\partial \theta_H}{\partial t} = \sum_{M=Si,Ge} \left(2 \frac{S_{MH_4} F_{MH_4}}{N_s} \theta_{nbl}^2 + 2\nu_{MH_3} \theta_{MH_3} \theta_v + 2\nu_{MH_2}^{(2)} \theta_{MH_2} \theta_v \right) - \nu_H (x) \theta_H, \ (7)$$

$$\frac{\partial \theta_M}{\partial t} = \nu_M \theta_M - r\theta_M,$$

$$\theta_v + \theta_{MH_3} + \theta_{MH_2} + \theta_{MH} + \theta_M + \theta_H = 1,$$

$$\theta_v = \theta_{bl} + \theta_{nbl},$$

$$\theta_{bl} = 3 \left(\theta_{SiH_3} + \theta_{GeH_3} \right).$$

The system (7) is based on the following considerations. (a) Monomolecular adsorption takes place on a growing layer surface. (b) Lateral interactions between atoms and molecules on a growth surface are absent. (c) Chemisorption of silane and germane molecules requires two vacant not blocked adsorption sites. (d) The GeH_3 and SiH_3 molecules block 3 vacant adsorption sites. (e) The desorption rate of hydrogen atoms from an alloy surface linearly depends on Ge content. (f) The frequency of atom embedding into a lattice (r) depends on concentration of atoms Si and Ge as described in [4]. Growth rate and Ge content of an alloy layer can be calculated by the formulas

$$x = \frac{\theta_{Ge}}{\theta_{Ge} + \theta_{Si}}, \ V = r\frac{N_s}{N_0} \left(\theta_{Si} + \theta_{Ge} \right).$$

2 Results and Discussion

Because the silane properties are investigated in more detail, we have focused the efforts on modeling of a growth from SiH_4. In order to define values of kinetic constants the experimental dependences of growth rate of layers on temperature [1, 5] and TPD spectra of hydrogen [2] have been used. As is visible from Fig. 1, the dependence $V(T)$ has a kink at the temperature about 620–630 °C. The $V(T)$ slope above this temperature is small and the activation energy approximately equals 0.1 eV. Such a value of the activation energy correlates well with the activation energy of disintegration of SiH_3 molecules [2]. Thus, the increase of the growth rate at $T > 620-630$ °C is limited by the disintegration of SiH_3 molecules. The fitting of the theoretical dependencies $V(T)$ to experimental data has allowed to determine the disintegration frequency of SiH_3
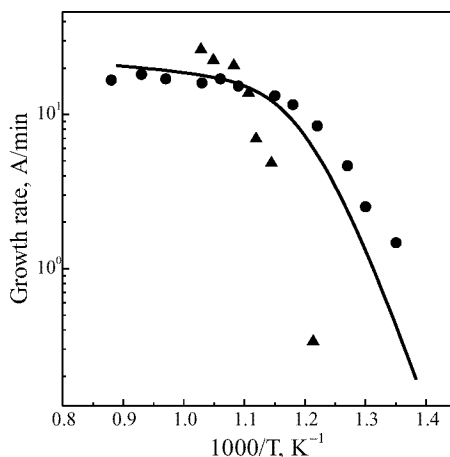
Fig 1. Experimental (curve) and theoretical (triangles — [1], circles — [5]) growth-temperature dependencies of the growth rate.
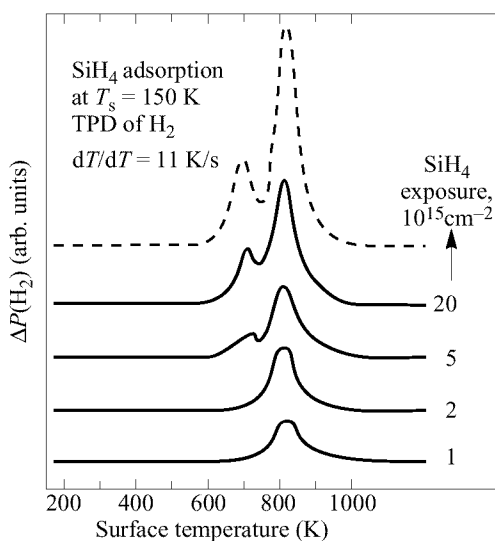

Fig 2. TPD data showing hydrogen desorption for silane adsorbed on the Si(100) [2].

molecules $\nu_{MH_3} \simeq 2.5 \times 10^0 e^{-0.087(eV)/kT} (s^{-1})$. This result coincides with conclusions of S. M. Gates with co-workers [2].

The definition of disintegration frequencies of SiH_2 molecules is a more difficult task. The difficulty consists in the fact that the disintegration of these molecules proceeds by two ways simultaneously. In order to determine these parameters, we have used TPD spectra of hydrogen [2]. As is visible from Figs. 2 and 3, these spectra have two maxima at 700 and 800 °C. The occurrence of the first desorption maximum is caused by reaction between two SiH_2 molecules, the second maximum is connected with the simple hydrogen desorption from the Si(100) surface. Fitting the first peak we have
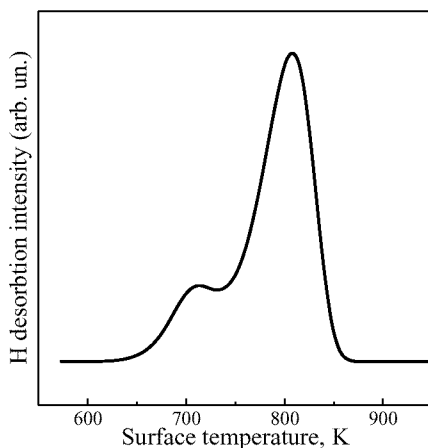
Fig 3. Calculated hydrogen TPD spectrum for silane adsorbed on the Si(100).

found $\nu_{MH_2}^{(1)} \simeq 5 \times 10^{17} e^{-2.5(eV)/kT}\,(\text{s}^{-1})$. The fitting of the second peak has allowed to specify the frequency of hydrogen desorption from the Si (100) surface ($\nu_H \simeq 8 \times 10^{12} e^{-2.13(eV)/kT}\,(\text{s}^{-1})$). The second peak has one feature: the low temperature half of the peak is narrower than the high-temperature one. The extension of this peak in the high temperature field is apparently connected with the monomolecular reaction (4). For the kinetic constant of this reaction we have found $\nu_{MH_2}^{(2)} \simeq 5 \times 10^2 e^{-0.6(eV)/kT}\,(\text{s}^{-1})$.

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